

SHEMYAKIN, M.M. : MAYMIND, V.I.

Reaction mechanism of osazone formation. Dokl. AN SSSR 102 no.6:  
1147-1150 Je'55. (MIRA 8:10)

1. Chlen-korrespondent Akademii nauk SSSR (for Shemyakin) 2. Institut biologicheskoy i meditsinskoy khimii Akademii meditsinskikh nauk SSSR  
(Osazones) (Chemical reaction--Mechanism)

PAUSON, Peter L.; KHOKHLOV, A.S., kandidat khimicheskikh nauk [translator];  
SHEMYAKIN, M.M., redaktor; ZAKHAL'YEVSKIY, V.A., redaktor;  
GERASIMOVA, Ye.S., tekhnicheskii redaktor

[Chemistry of tropones and tropolones. Translated from the English]  
Khimiia troponov i tropolonov. Perevod s angliiskogo A.S.Khokhlova.  
Pod red. M.M.Shemiakina. Moskva, Izd-vo inostrannoi lit-ry, 1956.  
204 p. (MLBA 9:7)

1. Chlen-korrespondent AN SSSR (for Shemyakin)  
(Tropones) (Tropolones)

RODIONOV, V.M., akademik, redaktor [deceased]; KAZANSKIY, B.A., akademik, redaktor; KNUNYANETS, I.L., akademik, redaktor; SHEMYAKIN, M.M., redaktor; MEL'NIKOV, N.N., professor, redaktor; TAYTS, S.Z., redaktor; SHEMASTINA, Ye.V., redaktor; KORNEYEVA, V.I., tekhnicheskiy redaktor

[Reactions and methods of analysis of organic compounds] Reaktsii i metody issledovaniia organicheskikh soedinenii. Moskva, Gos. nauchno-tekhn. izd-vo khim. lit-ry. Vol.4. 1956. 319 p. (MLBA 9:7)

1. Chlen-korrespondent AN SSSR (for Shemyakin)  
(Chemical reactions) (Isomers and isomerization)

SHEMYAKIN, M. M.

Advances of chemistry of antibiotics in recent years.  
A. S. Khokhlov and M. M. Shemyakin. *Khim. Nauki i  
Prom.* 1, 377-93(1956). A review with 251 references of  
the progress made in detn. of structures of antibiotics in-  
cluding those of acyclic structures, tropolone derivs., aroma-  
tic derivs., chloromycetin, quinone derivs., O- and V-hetero-  
cyclic derivs., streptomycins, polypeptides, chromopeptides  
and several antibiotics whose structures are as yet incom-  
pletely established. The literature coverage includes 1955.  
C. M. Kosolapoff

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SHEMYAKIN, M. M.

According to the article, "Investigation in the Field of Sarcomycin and Its Analogs. I. Synthesis of Dihydrocarbomyecin and Its Antipodes," by M. M. Shemyakin et. al., of the Institute of Biological and Medical Chemistry, Academy of Sciences USSR, Japanese chemists discovered sarcomycin in 1954. The structure of this antibiotic was worked out, however, by a group of American scientists in the latter part of 1955. This compound is known to have antibacterial properties and is active against tumors. The American scientists also discovered that reduced sarcomycin, i. e., dihydrocarbomyecin, has the same activity against tumors as the antibiotic itself.

Soviet scientists started seeking routes to the synthesis of sarcomycin and its analogs toward the end of 1955. The present report constitutes the first publication of the results of this research. The authors studied and developed a new synthesis of the racemates of cyclopentanone-3-carboxylic and 2-methylcyclopentanone-3-carboxylic acids. The latter of these acids was separated into optically active antipodes, one of which is identical to dihydrosarcomycin. (Zhurnal Obshchey Khimii, Vol 27, No 3, Mar 57, pp 742-748) (U)

94M. 1317

APPROVED FOR RELEASE: 08/23/2000 CIA-RDP86-00513R001549020019-0  
MAYMIND, V. I., TUKARYEV, B. V., VDOVINA, P. G., YEREMAYEV, K. M.,  
SHEMYAKIN, M. M.

Ref Zhur-Khimiya, No 4, 1957.

Investigation in the Field of Compounds, marked C14 and N15 IV. Synthesis of Key Compounds.

Zh. obshch. Khimii, 1956, 26, No 7, 1962-1967.

Abstract: Described are methods of synthesis of phthalimide-N15 (I); of potassium salt of phthalimide-N15 (II); HN1503 (III), Hcl4N; salts of III-HN1502 and HC 14N. 10-150 mols HN15H3 (from 0.1 Mole HN15H4NO3) are passed for 3 hours into a suspension of 0.015 mole of phthalic acid in 400 cc water the solution is evaporated, the remainder is heated (2000) and sublimated (290-300°); then it is ground with water and neutralized with a 5% solution soda, yield is 1, 98-99%. To a hot solution of 0.1 mole I is 350 cc anhydr., alcohol is added 50 cc 2N C2H5OK, yield is II, 98-99%, 0.15 mole HN15H3 and 0.12, HNO2 is separated, the filtrate is evaporated to 250-300 cc, neutralized with 20% H2SO4, evaporated to dryness, and after adding 70 cc H2SO4, (d 1.5) III is distilled off. By neutralizing III with alkalies the nitrates with a yield 82-84% are obtained. By the reduction of 0.01-0.05 mole HN1502 (or HN1503) by means of 0.015-0.075 g-atom Pb at 390° (for the preparation HN1502-at 330°) HN1502: yield 91-93% is obtained. Hcl4N is obtained with a yield 92-94% by a method described earlier (Maymind, V. I., Tukaryev, B. V. Shemyakin, M. M.

Dokl. AN SSSR, 1954, 81, 195), by heating (750-760°) BaCl<sub>2</sub>·3K and KI<sub>2</sub> in a current of H<sub>2</sub> and subsequent neutralization with H<sub>2</sub>SO<sub>4</sub>. In order to obtain KCl·H the vapors of HCl·H are passed through CaCl<sub>2</sub> at 40° absorbed by anhydro. alcoholat -250, and precipitated with a solution of C<sub>2</sub>H<sub>5</sub>OK or spontaneously absorb HCl·H with solution of an alcoholate. The previous reports see RZhKhim, 1956, 1961.

RELEASE: 08/23/2000

CIA-RDP86-00513R001549020019-2

USSR/Organic Chemistry. Synthetic Organic Chemistry.

Abs Jour: Ref Zhur-Khimiya, No 6, 1957, 19284.

Author : Maymind V. I., Ermolayev Y. M., Shemyakin M.M.

Inst : Investigations in the Field of Compounds marked C14 and

Title : H15. V. Synthesis of -H15 amino acids.

Orig Pub: Zh. obshch. khimii. 1956, 26, No 8, 2313-2318.

Abstract: The synthesis of -H15-aminoacids by condensation of phthalimide-H15-potassium (I) with the corresponding methyl esters of α-bromoacids (MEB) and hydrolysis of the obtained phthaloyl derivatives (PD) with a mixture of CH<sub>3</sub>COOH and HBr is described. By the action of CH<sub>2</sub>N<sub>2</sub> on the corresponding bromoacids MEB are obtained: α-bromo-6-N-benzoylaminovaleric acid, m.p. (0-61° (purification - by washing with ether at -10°); α-bromo-6-N-phthaloylaminovaleric acid m.p. 61-62° (from ether);

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α-benzoylaminovaleric acid, m.p. 43-44°  
α-bromo-6-N-phenylpropionic  
α-bromo-6-N-phenylpropionic

NESMEYANOV, A.N.; KNUNYANTS, I.L.; ~~SE~~ RMYAKIN, M.M.; BOGOSLOVSKIY, B.M.;  
SKURATOV, S.M.; KONKIN, A.A.; ~~DEREVITSKAYA~~, V.A.; ROGOVIN, Z.

In memory of A.A. Strepikheev; obituary. Zhur.ob.khim.26 no.11:3224-  
3226 N '56. (MLRA 10:1)  
(Strepikheev, Aleksandr Aleksandrovich, 1912-1955)

Shemyakin, M. M.

✓ Synthesis of  $\alpha$ -substituted  $\alpha$ -amino acids and their derivatives. M. M. Shemyakin, E. S. Chagan, and L. I. Denisov. *Bull. Acad. Nauk S.S.S.R.* 106, 676-8 (1958).

To 5 g. 2-phenyl-5-oxazolindione (I) in dry  $(CH_2Cl)_2$  was added at 5° 2.5 g.  $Br_2$  in  $(CH_2Cl)_2$ ; the ppt. of  $HCl$  rapidly sep'd. and the filtrate treated with dry ROH 1 hr. at room temp. gave the following:  $BzNHCH(OMe)CO_2Me$ , m. 86-7° (from Et<sub>2</sub>O);  $BzNHCH(OEt)CO_2Et$ , m. 69-71° (from 70% EtOH);  $BzNHCH(OPr)CO_2Pr$ , m. 54-5° (from 70% EtOH);  $BzNHCH(OC_4H_9)CO_2C_4H_9$ , m. 52-3° (from MeOH);  $BzNHCH(OCMe_3)CO_2CMe_3$ , m. 80-1° (from 70% EtOH);  $BzNHCH(OCH_2Ph)CO_2CH_2Ph$ , m. 136-7° (from MeOH);  $BzNHCH(CH_2Ph)CO_2CH_2Ph$ , m. 95-6° (from EtOH);  $BzNHCH(C_6H_5)CO_2C_6H_5$ , m. 118-19° (from MeOH). The reaction with PhOH gave  $BzNHCH(OH)CO_2Ph$ , m. 159-60° (from MeOH). If after the bromination, the reaction with MeOH is run at 18-20° 5 hrs. the product from 4-methyl-2-phenyl-5-oxazolindione is  $BzNHCH(OMe)CO_2Me$ , m. 114-15° (from MeOH-Et<sub>2</sub>O). The procedure outlined above with I applied to abs. Me<sub>2</sub>COH gave 23% II and 99%  $BzNHCH(OCMe_3)CO_2H.H_2O$  (III), m. 103-4° (from 70% EtOH), along with 89%  $BzNHCH(OH)CO_2CMe_3$ , m. 125-6° (from 70% MeOH); if use is made of Me<sub>2</sub>COH contg. 3.1% moisture, there is obtained 48% III. III on further heating solidifies at 140° and remelts at 201° (decomp.). The brominated I, prep'd. as above, treated at 0° with 0.27 g.  $H_2O$  and 8 ml. dioxane, followed by 3.4 g.  $PhCH_2OH$  1.5 hrs. at 20°, gave  $BzNHCH(CO_2H)OCH_2Ph$ , m. 123-5° (from 70% EtOH). Bromination of I followed by reaction with 1.7 g.  $PhCH_2OH$  1 hr. at 0° gave  $BzNHCH(OEt)CO_2CH_2Ph$ , 31%, m. 125-6° (from 70% EtOH); if the mixt. is then treated with  $PhNH_2$ , 1/2



**SHEMYAKIN, M. CHAMAN, F.**  
 2 hrs. at 0° there is formed 29%  $BzNHCH(NHPh)CO-$   
 $CH_2Ph$ , m. 158-7° (from MeOH); piperidine gave 3%  $Bz-$   
 $NHCH(NC_4H_9)CO_2CH_2Ph$ , m. 76-8° (from 70% MeOH).  
 The use of MeCOH and PhNH<sub>2</sub> similarly gave 68%  $BzNH-$   
 $CH(NHPh)CO_2CM_2$ , m. 155-6°, while PhNH<sub>2</sub> alone gave  
 78%  $BzNHCH(NHPh)CONHPh$ , m. 163-4° (from MeOH).  
 Use of PhCH<sub>2</sub>SH gave 77%  $BzNHCH(SCH_2Ph)COSCH_2Ph$ ,  
 m. 103-4° (from MeOH).  
 G. M. Kosolapoff

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SHEMYAKIN, M.M.; RAVDEL', G.A.; CHAMAN, Ye.S.

Synthesis of peptides containing an  $\alpha$ -oxy- $\alpha$ -aminoacid residue.  
Dokl.AN SSSR 107 no.5:706-709 Ap '56. (MLBA 9:8)

1. Chlen-korrespondent AN SSSR (for Shemyakin); 2. Institut biologicheskoy i meditsinskoy khimii Akademii meditsinskikh nauk SSSR.  
(Peptides)

USSR/ Physical Chemistry - Molecule. Chemical Bond.

B-4

Abs Jour : Referat Zhur - Khimiya, No 3, 1957, 7233

fractional contribution of  $\pi$ -electron interaction energy to the total BH energy in percent (fourth number in parentheses), and the interatomic O...H distance calculated from standard bond dist. and the bond angles (fifth number in parentheses in A.U.) have been determined for the following compounds: the vapor of the monomethyl ether of ethylene glycol (I) at 120-122° (3665, 0, 0, 0, -); I in CCl<sub>4</sub> (II), in the ratio 1:400 (3605, 60, 0.96, 0, 1.80); phenol in II, 1:400 ratio (3605, 0, 0, 0, -); guaiacol in II, 1:400 (3530, 55, 0.90, 0, 2.20); oxyoctenol in II, 1:400 (3475, 147, 2.38, 59.7, 1.95); benzoin in II, 1:400 (3468, 147, 2.39, 60.0, 1.95); 2-hydroxy-1, 4-naphthoquinone in II, 1:400, 3398 (187, 3.07, 68.7, 2.25); 2-benzyl-3-hydroxy-1, 4-naphthoquinone in II, 1:600 (3395, 190, 3.11, 69.1, 2.25); 2-(1-naphthyl)-3-hydroxy-1, 4-naphthoquinone in II, 1:600 (3370, 215, 3.52, 72.7, 2.25); 3-methyltropinone in II, 1:400 (3116, 504, 8.19, 88.2,

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APPROVED FOR RELEASE: 08/23/2000  
USSR/ Physical Chemistry - Molecule. Chemical Bond.

CIA-RDP86-00513R001549020019-0

Abs Jour : Referat Zhur - Khimiya, No 3, 1957, 7233

2.25); vapor of the monomethyl ether of trimethylene glycol (III) at 160° (3650, 0, 0, 0, -); III in II, 1:400 (3580, 70, 1.12, 0, 1.65); o-methoxybenzyl alcohol (IV) vapor at 163-164° (3652, 0, 0, 0, -); IV in II, 1:400 (3585, 67, 1.08, 0, 1.65); diacetone alcohol in II, 1:400 (3524, 94, 1.52, 26.2, 1.65); methoxybenzoic acid in II, 1:400 (3357, 228, 3.74, 70.0, 1.65); salicylic acid vapor at 144° (3265, 320, 5.25, 78.7, 1.65); salol in II, 1:400 (3230, 355, 5.82, 80.7, 1.65); methyl salicylate in II, 1:400 (3205, 380, 6.23, 82.0, 1.65); acetylacetone in II, 1:400 (3050, 570, 9.26, 87.9, 1.65); monomethyl ether of 1, 8-dihydroxynaphthalene in II, 1:400 (3431, 189, 3.07, 63.5, 1.63); 9-hydroxy-1-methoxy-7-oxy-9-methyl-5,6,7,8-tetrahydroanthracene in II, 1:600 (3620, 0, 0, 0, -); 10-hydroxy-1-methoxy-7-oxy-9-methyl-5,6,7,8-tetrahydroanthracene in II, 1:400 (3423, 197, 3.20, 65.0, 1.63); 10-hydroxy-1-methoxy-9-methyl-

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"Synthese et Proprietes des Acides Amino et Substitutes," paper presented at  
the 16th International Congress of Pure and Applied Chemistry, Paris, 18-24 Jul 1957

SHEMYAKIN, M. M.

Oxidative-hydrolytic splitting of carbon-carbon bonds of  
organic molecules / M. M. Shemyakin and L. A. Shchukina  
(U.S.S.R. Acad. Sci., Moscow). *Quart. Revs.* (London)  
10, 281-82 (1958); cf. *C.A.* 50, 4101a. -- Review, over 65  
references. E. H.

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Shemyakin-M.M.

Chemistry of chloromycetin (levomycetin). VIII. Dependence of antimicrobial activity of chloromycetin on its structure and the mechanism of action of chloromycetin. M. M. Shemyakin, M. N. Kolosov, M. M. Levitov, K. I. Germanova, M. G. Karapetyan, Yu. B. Shvetsov, and E. M. Bamdas. *Zhur. Obshch. Khim.* 26, 773-82(1956); cf. C.A. 49, 16049h; 50, 3291c. — Biol. tests of several *N*-acyl derivs. of chloromycetin against *Staphylococcus aureus*, *Escherichia coli*, *Bacillus subtilis*, and *Vibrio fluorescens* were performed. The results indicate that the *p*-nitrophenyl group is important to the activity of the drug both through its electronic behavior and its polarizing action on the rest of the mol.; the geometric dimensions of this part of the mol. are not important in contrast to the import of geometric dimensions in the aminopropanediol portion of the mol. The NO<sub>2</sub> group can be shifted without loss of activity to other conjugated locations, and compds. with *p*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>N: N— or *p*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CH: N— linkages are highly active; compds. without the NO<sub>2</sub> group or those with it in unconjugated locations (*p*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CONH—) are inactive or weakly active. The biol. activity of chloromycetin analogs drops off in the series of the *p*-phenyl substituents: NO<sub>2</sub>, CN, CO<sub>2</sub>Me, Cl, SO<sub>2</sub>Me, SO<sub>2</sub>NH<sub>2</sub>. Geometry and polarization in chloromycetin are discussed at length. New analogs were prepd. By heating 6 g. DL-threo-1(*p*-nitrophenyl)-2-amino-1,3-propanediol (I), 7.2 g. Me  $\gamma, \gamma, \gamma$ -trichlorocrotonate, and 4 ml. iso-AmOH to 110° for 1 min., followed by treatment with

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NIH  
Full translation available /m

SHEMYAKIN, M.M. ...

EtOAc, gave 17% DL-threo-1(p-nitrophenyl)-2-(γ,γ,γ-trichloroacetyl-amino)-1,3-propanediol, m. 165-6° (from  $\text{CH}_2\text{CH}_2\text{Cl}$ ). I (6 g.) in 350 ml.  $\text{Et}_2\text{O}$  and 180 ml. 0.5N KOH treated with 6.1 g.  $\text{CCl}_3\text{CH}_2\text{CH}_2\text{COCl}$  (b.p. 97°) 0.5 hr. gave 87% DL-threo-1(p-nitrophenyl)-2-(γ,γ,γ-trichlorobutyrylamino)-1,3-propanediol, m. 118-17° (from  $(\text{CH}_2\text{Cl})_2$ ). D- or L-form of I (9 g.) similarly treated with  $\text{CHCl}_3\text{CH}_2\text{CH}_2\text{COCl}$  (b.p. 79-81°,  $n_D^{20}$  1.5155) gave 70-5% D-threo-1(p-nitrophenyl)-2-(γ,γ,γ-dichloroacetyl-amino)-1,3-propanediol, m. 84-5° (from EtOAc and  $(\text{CH}_2\text{Cl})_2$ ),  $[\alpha]_D^{25}$  -70.8° ( $\text{Me}_2\text{CO}$ ); L-threo analog, m. 84-5°,  $[\alpha]_D^{25}$  67.6° ( $\text{Me}_2\text{CO}$ ); DL-analog, prepd. by mixing the 2 isomers, m. 144-5°. I (6 g.) in 300 ml. dry dioxane was treated at 12-15° with 2.45 g.  $\text{CCl}_3\text{CHCH}_2\text{COCl}$  over 0.5 hr.; after 0.5-hr. shaking the mixture was filtered and concd. in vacuo, treated with EtOAc, washed with dil.  $\text{H}_2\text{SO}_4$  and 20% NaCl, and evapd., yielding 88% DL-threo-1(p-nitrophenyl)-2-(γ,γ-dichlorovinylacetamido)-1,3-propanediol (II) hydrate (from heptane and  $(\text{CH}_2\text{Cl})_2$  or EtOAc- $\text{ClCH}_2\text{CH}_2\text{Cl}$ ), m. 72-3°; the water of hydration is lost at 100° in vacuo. This (0.3 g.) in dry dioxane treated with 2 drops dry  $\text{Et}_3\text{N}$  and kept 46 hrs. gave 90% DL-threo-1(p-nitrophenyl)-2-(γ,γ-dichloroacetyl-amino)-1,3-propanediol, m. 144-5°. Identical with the above described. Refluxing II with 20% HCl 2 hrs. gave 87%  $\text{CCl}_3\text{CHCH}_2\text{CO}_2\text{H}$  and 91% I. G. M. Kosolapoff

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SHCHUKINA, L.A.; SHEMYAKIN, M.M.

Oxidative and oxidative-hydrolytic transformations of organic molecules. Part 27: Tautomeric transformations and properties of hydroxy- and chloroketocarboxylic acids. Zhur.ob.khim. 26 no.6: 1708-1713 Je '56. (MIRA 11:1)  
(Acids, Organic) (Tautomerizm)



Shemyakin, M. M.

oxidative and oxidative-hydrolytic transformations of aromatic amines. XVIII. Oxidative-hydrolytic transformations of nitro-substituted aromatic amines. Shemyakin, M. M., Potapovskiy, A. M., and M. M. Potapovskiy (Textile Inst., Moscow). *Zhur. Obshch. Khim.*, 19, 1949-50 (1950); cf. C.A. 51, 1920a. Coupling diazotized 2,4-(O<sub>2</sub>N)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NH<sub>2</sub> with 1,2-C<sub>6</sub>H<sub>4</sub>(OH)<sub>2</sub> gave deep red 1-(2,4-dinitrophenylazo)-2,4-dihydroxyphenylene (I), decomp. 282-8°. This refluxed under N in 8.5% aq. NaOH 7.5 hrs. gave 1.18 g. 2,4-(O<sub>2</sub>N)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>OH, 1.15 g. 5-nitro-1,2,3-benzotriazole, m. 208-9° (Ac. deriv., m. 148°), and mixed phthalic and phthalonic acids; the latter acid gave a decomposition of 2,4-(O<sub>2</sub>N)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NHNH<sub>2</sub> gave 88% 5,5'-dinitrophenylene, m. 142-3°, 13.7% 5-nitro-1,2,3-benzotriazole, decomp. 190-1°. 5.5% m-C<sub>6</sub>H<sub>4</sub>(NO)<sub>2</sub> and 1% 2,4-(O<sub>2</sub>N)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>OH. The latter formed in 22% yield when the reaction of the azoxybenzene deriv. dropping correspondingly to 88.5%. Coupling of 2,6-(O<sub>2</sub>N)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NH<sub>2</sub> (diazotized) with 1,2-C<sub>6</sub>H<sub>4</sub>(OH)<sub>2</sub> gave bright-red 1-(2,6-dinitrophenylazo)-2,4-dihydroxyphenylene, decomp. 178-5°. This refluxed under N in phosphate buffer at pH 9.17 15 hrs. gave only a small amt. of phthalic acid and a considerable amt. of tar. Thus, the 2,4-dinitro deriv. is relatively more stable than the 2,6-dinitro analog. The mechanism of oxidation is discussed. G. M. Kozlovskiy

SHEMYAKIN, M.M.; SHCHUKINA, L.A.

Theory of oxidative and hydrolytic conversions of organic molecules  
[with summary in English]. Biokhimiia 22 no.1/2:214-225 Ja-F '57.  
(MLRA 10:7)

1. Institut biologicheskoy i meditsinskoy khimii Akademii meditsin-  
skikh nauk SSSR, Moskva.

(CHEMISTRY, ORGANIC,

theory of oxidative-hydrolytic conversion of organic  
molecules, review (Rus))

Shemyakin, M.M.

Compounds labeled with carbon-14 and nitrogen-15.  
 VI. New method of study of dual reactivity and tautomerism. 1. Study of the triazene/(diazamine) system. M. M. Shemyakin, V. I. Malinina, and E. Gomes. *Zhur. Obshch. Khim.* 27, 1842-4 (1957). cf. *C.A.* 51, 4944h. Treatment of 7.35 g.  $N^4$ -phthalimide in 20 ml.  $H_2O$  with 30 ml. 30% NaOH at  $30^\circ$  followed by 2.8 ml. NaOBr from 2.8 ml. Br, 9 g. NaOH, and 25 ml.  $H_2O$  precooled to  $0^\circ$ , gradual cooling to  $0^\circ$  and acidification with HCl to pH 4, and addition of 10-15 ml. AcOH gave 80-85%  $N^4$ -anthranilic acid; this on pyrolysis gave  $PhN^4H_2$ . Diazotization of unlabeled  $PhNH_2$  in aq. HCl, addition of acetate buffer of pH 6.38, filtration if necessary, and addition of  $PhN^4H_2$  in MeOH gave 90% diazoaminobenzene, m.  $100^\circ$ , in which the label is on one of the end N atoms. Similar reaction of  $PhNH_2$  and  $NaN^4O_2$  gave diazoaminobenzene labeled at the middle N atom. Isomerization of these in AcOH (Rosenhauer and Unger, *C.A.* 22, 1761) gave aminoazobenzene, which was diazotized and decomd. in the presence of hydroquinone, or was thermally decomd. at  $150^\circ$ . The examn. of isotope distribution of N in the products shows that  $PhN:NNHPh$  is a nearly equimolar isomer mixt. with  $PhNNH:NPh$  and that the triazene system is highly mobile. The dual reactivity of the compd. is not connected with transfer of the reactive center from one N atom to another during reactions. Acylation with  $Ph_2C:O$  gave the *N*-diphenylacetyl deriv., decomp.  $143^\circ$ , whose decompn. indicated the equalization of isotope compn. of N on the terminal atoms of the triazene.  
 G. M. Kosolapoff

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 4E4j  
 4E3d  
 4E2c(j)  
 2-may  
 1-Rmg

SH-EMYAKIN, M. M.

Distr: 4E4j/4E3d/4E2c(j)

Mechanism of azoxy coupling reaction. M. M. Shemyakin, V. I. Malozemov, and B. K. Valchunovskiy. *Izv. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1957, 1280-2. To 0.5 g. PhNH<sub>2</sub> in 10 ml. EtOH was added at 10° 0.5 g. PhNO in EtOH, the mixt. treated with 0.8 ml. 7% alc. KOH and, after 2 min., neutralized with H<sub>2</sub>SO<sub>4</sub>, yielding 92% azoxybenzene/cortg. with N<sub>2</sub>. This was brominated (cf. Angell and Valori, C.A. 6, 1137) to 4-bromoazoxybenzene-N<sub>2</sub>, m. 73°, which heated with Sn-HCl and the crude product treated with Ac<sub>2</sub>O yielded 90% p-BrC<sub>6</sub>H<sub>4</sub>NHAc and 38% PhNHAc. The N<sub>2</sub> content in atom percent in these products was: 37.2 in PhNO, 19.1 in PhNHAc, and 18.2 in p-BrC<sub>6</sub>H<sub>4</sub>NHAc. Thus N<sub>2</sub> excess was distributed equally among the cleavage products, indicating the formation of an intermediate compd. with equiv. locations of the N atoms, such as (PhN<sup>2</sup>OH)<sub>2</sub>. G. M. K.

4  
3

11

SHEMYAKIN, M.M.; RANDEL', G.A.; CHAMAN, Ye.S.; SHVETSOV, Yu.B.; VINOGRADOVA,  
Ye.I.

Synthesis of racemic sarkomycin..Izv. AN SSSR. Otd. khim. nauk  
no.8:1007 Ag '57. (MIRA 11:2)

1. Institut biologicheskoy i meditsinskoy khimii Akademii meditsin-  
skikh nauk SSSR. (Sarkomycin)

TERENT'YEV, A.P.; YANOVSKAYA, L.A.; RUKHADZE, Ye.G., redaktor;  
RODIONOV, V.M., akademik, redaktor [deceased]; KAZANSKIY, B.A.,  
akademik, redaktor; KNUNYANTS, I.L., akademik, redaktor;  
SHEMYAKIN, M.M., redaktor; MEL' NIKOV, N.N., prof, redaktor;  
LUR'YE, M.S., tekhnicheskii redaktor.

[Polarographic analysis in organic chemistry] Poliarograficheski  
method v organicheskoi khimii. Moskva, Gos. nauchno - tekhn. izd-  
vo khim. lit-ry, 1957. 388 f. (Reaktsii i metody issledovaniia  
organicheskikh soedinenii, vol.5) (MIRA 10:10)

1.Chlen-korrespondent AN SSSR (for Shemyakin).  
(Polarography) (Chemistry, Organic)

Shemyakin, M.M.

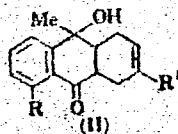
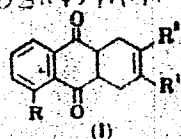
Initial stages of synthesis of tetracyclins. M. M. Shemyakin, M. N. Kolosov, M. G. Karapetyan, and B. S. Chumakov. *Doklady Akad. Nauk S.S.S.R.* 112, 689-72 (1957).  
Initial steps of the syntheses of the tetracycline group of antibiotics are reported. Condensation of 1,4-naphthoquinones with butadiene and its derivs. at 100° gave the following (I) (R, R', R" given): H, MeO, H, 23%, m. 143-4°; MeO, H, H, 91%, m. 92-3° (λ 229 and 338 mμ); AcO, H, H, 91%, m. 113.5-14.5° and 135.5-6.5°. The condensation of 6-methoxynaphthoquinone with CH<sub>2</sub>:CHC(OMe):CH<sub>2</sub> was run in C<sub>6</sub>H<sub>6</sub> under CO<sub>2</sub> 12 hrs. at 100° yielding 94% mixed isomers which gave 55% I (MeO, MeO, H), m. 144-5° (λ 227 and 338 mμ), and I (MeO, H, MeO), 16%, m. 141-3° (λ 221, 338 mμ), the structures of which were proved by oxidation to the dimethoxyanthraquinones, and hydrolysis to the dihydroxyanthraquinones, identified as the *diastereois.*, m. 197-8°, and 204-5°, resp. I in C<sub>6</sub>H<sub>6</sub> gradually treated with strong cooling with MeMgI (not over 25% excess) yielded II (R, R' given): H, H, 70%, m. 135-7° (λ 248 and 291 mμ); MeO, H, 12%, m. 194-6° (λ 239 and 317 mμ). I (MeO, MeO, H) gave 2 products: II (MeO, MeO), 12%, m. 191-3°, and IIa, 19%, m. 137.5-8.5°. The structures were proved by conversion to 1,9- and 1,10-hydroxymethoxyhydroanthracenes whose infrared spectra showed typical chelation of HO with MeO groups. Use of excess MeMgI and reversal of the order of addn. gives III (R and R' given): H, H, m. 160-7° (λ 238, 260, 285, and 297 mμ); H, MeO, 49%, m. 171-2°; MeO, H, 49%, m. 160-40° (λ 272 and 278 mμ). The ketols and the glycols were stable in air in contrast to the I;

4.4E4  
Kolosov, M. N.; K'arak Pet Van, M. G. + Chaman, E. S.

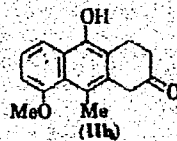
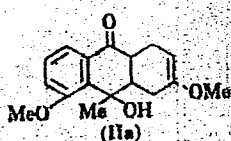
2/4  
this indicates a trans structure of the former compds. owing to epimerization of 1 of the asym. centers. The C-10-asym. center can be examd. on the basis of the postulates of Cram and Elhales (C.A. 48, 2648e), which lead to the Me group being cis in respect to the H on C-10a. Thus, II correspond geometrically to the natural tetacycline antibiotics. This is confirmed by acidic treatment of III which leads to their dehydration. Heating with aq. alc. HCl 0.5 hr. at 60° leads to dehydration to the following IV (R and Z given): R, CH:CH, 83%, m. 117-18° (acetate, m. 153-5°; Me ether, m. 97-9° (λ 236, 288, 297 mμ)); MeO, CH:CH, 96%, m. 115-16° (λ 241, 311, 334 and 339 mμ) (dihydro deriv., m. 107.5-8° (λ 237, 312, 324, and 339 mμ)). III (R = MeO, R' = H) gave 90% V (R = MeO, Z = CH:CH), m. 115-



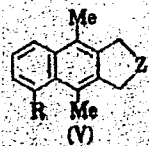
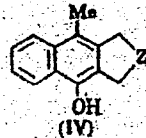
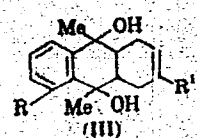
Kolosov, M. N., et al. V. P. Pavlov, M. G. Chaman, E. S.



4-4E43



3/4



Kolosov, M.N.; Kara Pet'yan, M.G. & Chumakov, E.S.

15.5° (λ 241, 298, 308, 319, and 333 mμ). The keto alcs. and the glycols, which are really enol deriva., are attacked by HCl under the above conditions yielding the corresponding ketones of the tetrahydroanthracene group. Thus II (R = R' = MeO) gave IV (R = MeO, Z = CH<sub>3</sub>CO), m. 138-7°, while IIa gave I(b, m. 170-3°. III (R = H, R' = MeO) gave 84% IV (R = H, Z = CH<sub>3</sub>CO), m. 120-1°. If the substance, however, is shaken in Et<sub>2</sub>O with 1-2% HCl at 20° only the MeO group of ring C is attacked. Thus, III (R = H, R' = MeO) give 63% 2-oxo-9,10-dihydroxy-9,10-dimethyl-1,2,3,4,4a,9a,10a-octahydroanthracene, m. 135-6°.

G. M. Kosolapoff

PM  
MT

4/4

The Tautomerism of Arylazotropolones.

20-3-29/59

in position 3. On this occasion they change into corresponding 5-ary-  
lazo-4-carboxylmethyl tropolones (VII); this reaction does not take  
place in the case of the initial tropolon (IIIg), in the case of the  
tautomeric models Vg-Ve, however, absolutely natural, where the se-  
paratable carboxyl group is in a  $\beta$ -position with respect to one of  
the carbonyl groups. Finally it was found that on the occasion of  
the transformation of the arylazotropolones IVg-IVe into acids (VII)  
and also directly from the latter, slightly neutral compounds (VIII)  
are formed as a consequence of closing the heterocycle of the tro-  
pochinonhydrazon forms of the arylazotropolones. The knowledge about  
the tropochinonhydrazon tautomerism of the arylazotropolones I  $\rightleftharpoons$  II  
which were obtained by chemical investigation could be confirmed  
spectroscopically. The capacity of the arylazotropolones for the a-  
bove discussed tautomerism was recently noticed by Nozoe who also  
observed the formation of the chinoxalin-derivates with o-phenylen-  
diamine. In the experimental part the usual data concerning the pro-  
duction methods and the constants of the substances in question are  
given. There is 1 table and 1 Slavic reference.

Card 2/2

ASSOCIATION

SUBMITTED  
AVAILABLE

Institute for Biological and Medical Chemistry of the Academy of  
Medical Sciences of the USSR and of the Moscow Textile Institute.  
(Institut biologicheskoy i meditsinskoy khimii Akademii meditsins-  
kikh nauk SSSR, Moskovskiy tekstil'nyy institut).  
June 17, 1957  
Library of Congress

RODIONOV, Vladimir Mikhaylovich, akademik [deceased]; ZVORYKINA, V.K.,  
sostavitel'; KISELEVA, V.V., sostavitel'; FEDOROVA, A.M.,  
[translator]; KNUNYANTS, I.L., akademik, otv.red.; SHEMYAKIN, M.M.,  
akademik, otv.red.; SHVETSOV, Yu.B., red.izd.; POLENOVA, T.P.,  
tekhn.red.

[Selected works] Izbrannye trudy. Moskva, Izd-vo Akad. nauk SSSR,  
1958. 792 p. (MIRA 12:2)  
(Chemistry, Organic)

SEEMYAKIN, M. M. (Moscow, USSR)

"Einige Wege zur Synthese von Tetracyclinen"

report submitted for IV Intl. Cong. of Biochemistry, Vienna, 1-6 Sept 1958.

SOV/62-58-6-34/37

AUTHORS: Shemyakin, M. M., Kolosov, M. N.,  
 Arbuzov, Yu. A., Onopriyenko, V. V.,  
 Shatenshteyn, G. A.

TITLE: The Course Taken by the Synthesis of Ring A of Tetracyclic  
 Compounds (Put'sintesa kol'tsa A tetratsiklinov)

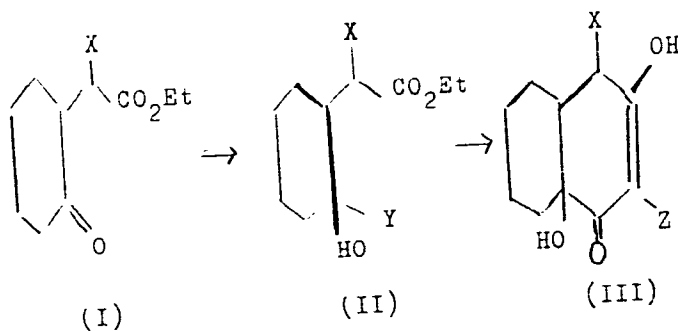
PERIODICAL: Izvestiya Akademii nauk SSSR, Otdeleniye khimicheskikh nauk, 1958,  
 Nr 6, pp. 794-795 (USSR)

ABSTRACT: Already in 1957 the authors of this report described the  
 synthesis of tricyclic compounds in which 2 rings, with respect  
 to their structure, resemble rings D and C of tetracyclic  
 compounds. The third ring, which corresponds to ring B,  
 contains a binary compound or a potential carbonyl group. At  
 present the authors are studying the possibility of synthesizing  
 ring A and describe this synthesis. The group  $\text{CHX} \cdot \text{CO}_2$  is  
 introduced into the initial ketone, ketone ester is  
 ethylated, ethynyl carbinol (formula III)  $\text{Y}=\text{C}\equiv\text{CH}$  is hydrated  
 in the neutral medium and oxy-ketoester (formula II;  $\text{Y}=\text{Ac}$ )  
 is cyclized into an oxy-diketone (formula III;  $\text{Z}=\text{H}$ ).  
 (Formula III;  $\text{Z}=\text{CONHR}$ ). The scheme has the following form:

Card 1/3

The Course Taken by the Synthesis of Ring A  
of Tetracyclic Compounds

30V/62-58-6-34/37



There are 2 references, 1 of which is Soviet.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR i Institut biologicheskoy i meditsinskoy khimii Akademii meditsinskikh nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy, AS USSR and Institute of Biological and ~~Medico-~~chemistry of the Academy of Medical Sciences of the USSR.)

Card 2/3

SCV/62-96-9-22, 26

AUTHORS: Shigorin, D. N., Shenyakin, M. N.,  
Kolosov, M. N.

TITLE: Intermolecular Interactions Between Acetylene and Its Derivatives  
(Mezhmolekulyarnyye vzaimodeystviya u atsetilena i yego  
proisvodnykh)

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk,  
1958, Nr 9, pp 1133 - 1134 (USCR)

ABSTRACT: Considering the peculiarities of the chemical structure  
of acetylene and its derivatives the authors considered it  
possible that these compounds might be able to form com-  
plexes with one another and with solvents. These complexes  
could result from the hydrogen bridge bonds  $R-C \equiv C-H \cdots X$   
( $X = O < , O = C < N < , -C \equiv C$ , and so forth). The study  
of the infrared absorption spectra showed frequency changes  
in the  $\equiv C-H$  and  $-C \equiv C-$  groups of acetylene and its  
derivatives in dissolving in acetone, ether, pyridine, and  
dioxane, in sublimating from the crystalline to the vapor  
state and in solutions of  $CCl_4$ . This probably means that  
the acetylene molecule forms complexes with the molecules

Card 1/3



Intermolecular Interactions Between Acetylene and Its  
Derivatives

SCV, 62-10-22, 26

of the solvent by forming hydrogen bonds. The union of the acetylene molecules and the homologs and derivatives of acetylene is apparently possible because of the electron shift in the  $\equiv C-H$  and  $-C\equiv C-$  bonds (which also belong to many other molecules). For this reason intermolecular electron orbitals are hypothesized. The authors discovered a new phenomenon in intermolecular interaction. It was shown experimentally that the formation of hydrogen bridge bonds and  $\pi$  complexes among the molecules of acetylene and its derivatives is possible. It was demonstrated that the hydrogen of the  $\equiv C-H$  group exchanges with deuterium in the dissolution of  $R-C\equiv CH$  compounds in  $CH_3OD$  or  $C_2H_5OD$ . For  $R-C\equiv CD$  in  $CCl_4$  the following frequencies were found:

$\nu(\equiv C-D) = 2600 \text{ cm}^{-1}$ ;  $\nu(-C\equiv C-) = 1957 \text{ cm}^{-1}$ . There is 1 table.

Card 2/3

Intermolecular  
Derivatives

Between Acetylene and Its

SDV/c2-05-9-22/21

ASSOCIATION: Fiziko-khimicheskiy institut im. L.Ya. Karpova (Physical-  
Chemical Institute imeni L.Ya. Karpov) Institut biologicheskoy i meditsinskoy khimii Akademii meditsinskikh nauk SSSR  
(Institute of Biological and Medical Chemistry of the Academy  
of Medical Sciences of the USSR)

SUBMITTED: June 24, 1958

Card 3/3

79-28-A-29/60

AUTHORS: Shenyakin, M. M. Maymind, V. I., Tokarev, B. V., Karpov, V. I.

TITLE: Investigation of Stofen's (Stefen) Reaction (Izucheniye reaktsii Stefena) (Report VII From the Series "Investigations in the Field of Compounds Marked by C<sup>14</sup> and N<sup>15</sup>". Previous Report See Reference 1)

PERIODICAL: Zhurnal Obshchey Khimii, 1958, Vol. 28, No. 4, pp. 976-983 (USSR)

ABSTRACT: In the investigation of the synthesis of amino acids marked by radioactive carbon the authors had to apply Stofen's reaction for the production of aliphatic aldehydes from corresponding nitriles. As so far Stofen's reaction in this case provided not very satisfactory results, the authors were forced to settle the best conditions of its development at the example of the production of one of the aldehydes of the aliphatic series (iso-valeric anhydride). Later these conditions were also extended to the synthesis of other aldehydes - acetaldehyde and phenylacetaldehyde. The following was ascertained as a result of the investigations: 1) The salt of the aldimine and of the hexachloro stannic acid, which develops immediately

Card 1/3

79-23-4-29/60

Investigation of Steffen's (Stefen) Reaction. (Part II) From the Series  
"Investigations in the Field of Compounds Marked by G<sup>1</sup> and N<sup>1</sup>". Previous  
Report See Reference 1)

during the reaction can be dissolved in the reaction medium up to a certain degree. The salt of the phenyl-acetaldehyde entirely deposits as sediment, whereas the salt of the acetaldehyde partly remains in solution, and the salt of the iso-valeric aldehyde dissolves entirely. For this reason in Steffen's reaction in every new case not only the sediment but also the residue after the separation of the solvent must be investigated. 2) The best reaction temperature is in the range of 15 to 25°C (Table 1). 3) The optimum duration of the reduction reaction is 7 days (Table 2). 4) The best quantity of stannous chloride in the production of the iso-valeric aldehyde is 7 moles to 1 mole of nitryl (Table 3). 5) Presence of water in the reaction medium effects a diminution in the yield of aldehydes (Table 4). As a result of the investigations it has been ascertained that the yield of iso-valeric aldehyde under the best conditions is 61 - 64 %, of acetaldehyde 64 - 67 % and of phenylacetaldehyde 55 - 60 %. It has been shown that the transformation reaction of nitryls into imino ethers competes with the reduction

Card 2/3

Investigation of Steffen's (Stefen) Reaction. (Report VII From the Series  
 "Investigations in the Field of Compounds Marked by C<sup>14</sup> and H<sup>15</sup>". Previous  
 Report See Reference 1)

79-28-4-29/60

reaction of nitryls to aldimines. The transformation re-  
 action takes place under the influence of alcohol de-  
 veloped in consequence of the decomposition of ethyl ether  
 by hydrogen chloride. At higher temperatures this process  
 can entirely prevent the reduction of nitryl. Starting from  
 KC<sup>14</sup>, the reduction of benzilcyanide to phenylacetaldehyde  
 after Steffen was used for the synthesis of the phenyl-  
 alanine-2-C<sup>14</sup>. There are 4 tables and 26 references, 4 of  
 which are Soviet.

ASSOCIATION: Institut biologicheskoy i meditsinskoy khimii Akademii  
 meditsinskikh nauk SSSR (Institute for Biological and Me-  
 dical Chemistry of the Academy of Medical Sciences USSR)

RECEIVED: March 12, 1957

REF ID: A61170

AUTHORS: ~~Shenyakin, M. M.~~, Maymind, V. I.  
Vaychunayte, B. K.

504/79-28-6-61/63

TITLE: Letters to the Editor (Pis'ma v redaktsiyu) Investigation of the Wallach Regrouping and Its Related Reactions (Izucheniye peregruppirovki Vallakha i rodstvennykh yey reaktsiy)

PERIODICAL: Zhurnal obshchey khimii, 1958, Vol. 28, Nr 6, pp. 1708 - 1709 (USSR)

ABSTRACT: Lately the authors explained the reaction mechanism of the azoxy binding by means of  $N^{15}$  (Ref 1) and found that this process takes place through the stage of formation of the intermediate dioxy compounds. At present they use  $N^{15}$  for the investigation of various isomerizations of azoxy compounds - of the Wallach regrouping and of its related reactions. For this purpose the  $C_6H_5N^{14}(O) \rightleftharpoons N^{15}C_6H_5$  (Refs 2,3) was synthesized from  $C_6H_5N^{15}H_2$  and  $o-O_2N^{14}C_6H_4CHO$ ; the product was then subjected to a regrouping into the o- and p- oxyazobenzenes on different conditions. The isotopic composition of the nitrogen in azoxybenzene was determined by bromination and subsequent reduction cleavage (Ref 1),

Card 1/3

Letters to the Editor. Investigation of the Wallach 304/79-28-6-61/63  
Regrouping and Its Related Reactions

and in the oxyazobenzenes by reduction with tin in concentrated hydrochloric acid at 85-90°. It was found that in the presence of chlorosulfonic acid (Ref 4) the regrouping of azoxybenzene into the p-oxyazobenzene is accompanied by a complete balance of the isotopic composition of either nitrogen. On the action of 83% sulfuric acid on azoxybenzene the same results were obtained, which does not agree with the statements in publications. From the experiments carried out for this purpose follows that the conversion of the azoxybenzene into the p-oxyazobenzene takes place in two different ways: in the one way - the main way mentioned in scheme 1 - this regrouping takes place through the stage of oxide formation, and in the other way - the secondary way mentioned in scheme 2 - it takes place without touching this stage. The regrouping under the influence of ultraviolet light was only little accompanied by the balance of the isotopic composition of the nitrogen of the o-oxyazobenzene (Scheme 3). There are 5 references, 2 of which are Soviet.

Card 2/3

Letters to the Editor. Investigation of the Wallach SOV/ 79-28-6-61/63  
Regrouping and Its Related Reactions

ASSOCIATION: Institut biologicheskoy i meditsinskoy khimii ~~Academi meditsinskikh nauk~~  
SSSR (Institute of Biological and Medical Chemistry, Academy of  
Medical Sciences USSR)

SUBMITTED: February 24, 1958

1. Azoxybenzene--Synthesis

Card 3/3



SOV/79-28-8-15/66

IN 10071:

Shemyakin, M. M., Kolosov, N. N., Karapetyan, N. G.,  
Podionov, V. Ya.

TITLE:

Investigations on Sarcomycin and Its Analogs (Issledovaniya  
v oblasti sarkomitsina i yego analogov) II. Synthesis of the  
Sarcomycin Isomer (II. Sintez izomera sarkomitsina)

SYNOPSIS:

Zhurnal obshchey khimii, 1958, Vol. 28, Nr 6, pp. 2068-2074  
(USSR)

ABSTRACT:

In connection with a previous publication on sarcomycin (Ref 1)  
the authors worked on synthesizing this antibiotic (Formula I)  
and its ethyl ester isomer (II), which differs from sarcomycin  
in the positions of its methylene groups. Although sarcomycin  
has a simple structure its synthesis is especially difficult  
because it is easily oxidized and has a tendency to polymerize  
and to form isomers. Therefore, an energetic reaction cannot  
be carried out, and only mild reagents and lowered reaction  
temperatures can be used. Since the characteristic 8-methylene-  
 $\gamma$ -keto-acid group in sarcomycin cannot stand strong treatment  
the splitting of quaternary ammonium salts of the type

Class 1/3

Investigations on Sarcomycin and Its Analogs.  
 III. Synthesis of the Sarcomycin Isomer

SOV/79-28-6-15/66

$-\text{COCH}(\text{CH}_2\text{NR}_3^+)-$  seemed to be a promising synthetic method. One can synthesize in various ways the compounds of type (III) necessary for producing sarcomycin. The simplest way to synthesize these compounds was to use the easily obtainable cyclopentanone-3-carboxylic acid (IV), by introducing the dialkyl aminomethyl group into the 2 position by the Mannich reaction and then halogenalkylating the resulting tertiary amine. The synthesis of the isomer of the antibiotic sarcomycin (which is used against malignant tumors) was accomplished in this way. The starting material was cyclopentanone-3-carboxylic acid. This compound was condensed with formaldehyde and piperidine. The next steps were esterification and iodomethylation, and the end-product was then converted to the corresponding quaternary ammonium salt. The splitting of the salt yielded the ester of the iso-sarcomycin. There are 10 references, 2 of which are Soviet.

ASSOCIATION: Institute biologicheskoy i meditsinskoy khimii Akademii meditsinskikh nauk SSSR (Institute of Biological and Medical Chemistry of the Academy of Medical Sciences, USSR)

Card 4/5

PHASE 1: BOOK EXPLOITATION

SOV/3494

Reaktsii i metody issledovaniya organicheskikh soyedineniy, Kn. 8 (Reactions and Research Methods of Organic Compounds, Bk. 8) Moscow, Goskhimizdat, 1959. 446 p. Errata slip inserted. 4,200 copies printed.

Eds (Title page): V.M. Rodionov, Academician (Deceased), B.A. Kazanskiy, Academician, I.L. Knunyants, Academician, M.M. Shemyakin, Academician, and N.N. Mel'nikov, Professor; Ed. (Inside book): V.P. Yevdakov; Tech. Ed.: V.F. Zazul'skaya.

PURPOSE: This book is intended for laboratory personnel at industrial plants, for instructors and students at higher educational establishments, and particularly for scientists and researchers working at the numerous research institutes in the Soviet Union.

COVERAGE: This is the eighth volume in a series "Reactions and Research Methods of Organic Compounds." This series does not duplicate the one published in English under the title "Organic Reactions" and appearing in Russian translation; however, some material, of particular interest, is included in this publication. The present series is primarily devoted to reviewing the works of Soviet chemists. The eighth volume of this series deals with thiocyanation

Card 1/5

5(3)

AUTHORS:

Shemyakin, M. M., Denisova, L. I.,  
Chaman, Ye. S.

SOV/62-59-4-19/42

TITLE:

Investigations in the Field of the  $\alpha$ -Substituted  $\alpha$ -amino Acids  
(Issledovaniya v oblasti  $\alpha$ -zameshchennykh  $\alpha$ -aminokislot).  
Communication 5. Methods of Preparing Substituted  $\alpha,\alpha$ -Diamino-  
carboxylic Acids (Sobshcheniye 5. Sposoby polucheniya zame-  
shchennykh  $\alpha,\alpha$ -diaminokarbonovykh kislot)

PERIODICAL:

Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk,  
1959, Nr 4, pp 690-694 (USSR)

ABSTRACT:

In the present work it has been confirmed that various  
 $\alpha,\alpha$ -diamino acids can easily be obtained in the form of deriv-  
atives by the method recently proposed (Refs 20-23). This  
has made the production of many of these acids possible. It  
has been found that a quick reaction of the aniline used in  
the reaction (aniline, benzylamine, piperidine) with the  
oxazolinone ring makes it possible for this amine to act  
directly on the intermediate product, bromooxazolinine (III).  
This gives the corresponding amides of  $\alpha$ -amino- $\alpha$ -acylamino-  
carboxylic acids of type (IV) in a good yield (Schemes (I)  $\rightarrow$   
(II)  $\rightarrow$  (III)  $\rightarrow$  (IV) and Tables 1 and 2).

Card 1/3

Investigations in the Field of the  $\alpha$ -Substituted SOV/62-59-4-19/42  
 $\alpha$ -Amino Acids. Communication 5. Methods of Preparing Substituted  
 $\alpha, \alpha$ -Diaminocarboxylic Acids

If the amine used opens the oxazolinone ring only slowly, secondary reactions (polymerization, resinification) are observed, whereby the yield of the final compound is reduced. In some cases (IV) cannot be precipitated at all in individual form (Table 1). In these cases the oxazolinone ring must be opened first by another reagent. The corresponding esters of  $\alpha$ -amino- $\alpha$ -acylamino-carboxylic acids (VI) can be synthesized in a satisfactory yield if 1 mole of any alcohol (or mercaptan) is previously caused to act on bromooxazolinone (III). These compounds may also be synthesized with such amines (aniline, benzylamine, piperidine, etc) as are suitable for the synthesis of amides of type (IV). (Schemes (I)  $\rightarrow$  (II)  $\rightarrow$  (III)  $\rightarrow$  (V)  $\rightarrow$  (VI) and Table 2). It must be mentioned that this reaction is accompanied by secondary conversions in some cases. Another synthesis of the substituted  $\alpha, \alpha$ -diamino-carboxylic acids has been found during an investigation of the properties of  $\alpha$ -hydroxy- $\alpha$ -acylamino acids (VIII). It has been found that these acids can be converted into  $\alpha, \alpha$ -di-(acyl-amino) acids (IX) when heated with acid amides. Some of these

Card 2/3

Investigations in the Field of the  $\alpha$ -Substituted  $\alpha$ -Amino Acids. Communication 5. Methods of Preparing Substituted  $\alpha,\alpha$ -Diaminocarboxylic Acids SOV/62-59-4-10/42

acids have been synthesized by this method (Table 2). There are 2 tables and 26 references, 8 of which are Soviet.

ASSOCIATION: Institut biologicheskoy i meditsinskoy khimii Akademii meditsinskikh nauk SSSR (Institute of Biological and Medical Chemistry of the Academy of Medical Sciences, USSR), Moskovskiy tekstil'nyy institut (Moscow Textile Institute)

SUBMITTED: July 13, 1957

Card 3/3

5(3)

AUTHORS:

Shemyakin, M. M., Shigorin, D. M.,  
Shchukina, L. A., Semkin, Ye. P.

SOV/62-59-4-20/42

TITLE:

Structure and Mechanism of the Hydrolytic Splitting of  
 $\alpha$ -Nitro- $\alpha$ -Phenylacetophenon o-Carboxylic Acid (Stroyeniye i  
mekhanizm gidroliticheskogo rasshchepleniya  $\alpha$ -nitro- $\alpha$ -fenil-  
atsetofenon-o-karbonovoy kisloty)

PERIODICAL:

Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk,  
1959, Nr 4, pp 695-698 (USSR)

ABSTRACT:

To determine the structure of  $\alpha$ -nitro- $\alpha$ -phenylacetophenone-o-carboxylic acid and its salts the spectra of these compounds were investigated in the present work (Table 1). These investigations have provided an answer to the question relating to their structure and their different behavior in the presence of hydrolyzing agents. As was to be expected,  $\alpha$ -nitro- $\alpha$ -phenylacetophenone-o-carboxylic acid, like other aromatic o-aldehyde-(keto)-acids, has the structure of lactol (IIIb) rather than that of the keto acid (IV) in the crystalline state as well as in solution. After the actual structure of the  $\alpha$ -nitro- $\alpha$ -phenylacetophenonic acid and of its disodium salt had been clarified, its different behavior in the

Card 1/3

Structure and Mechanism of the Hydrolytic Splitting of SOV/62-59-4-20/42  
 $\alpha$ -Nitro- $\alpha$ -Phenylacetophenone -o-Carboxylic Acid

presence of hydrolyzing agents has been understood. As was shown before (Ref 3) the C-C bonds can split in those compounds in which a prototropic group (V) is present or can be formed in the molecule. The tendency to split depends directly on the degree of polarization of the C-C bond under the action of the substituent.  $\alpha$ -Nitro-dinitrophenylacetophenone-o-carboxylic acid itself, having a lactol (IIIb) structure, does not only contain the required group (V) but also a nitro group which can polarize the splitting bond to a very high degree in the required direction. For this very reason the acid (IIIb) splits easily to form phthalic acid anhydride and phenylnitromethane if the pH-value of the solution exceeds 7. In the molecule of the disodium salt, on the other hand, the prototropic group (V) is not contained nor can it be formed by hydration owing to the structure of this salt. This fact is responsible for the resistance of this compound to hydrolytic splitting. There are 1 table and 11 references, 8 of which are Soviet.

Card 2/3



Structure and Mechanism of the Hydrolytic Splitting of SOV/62-59-4-20/42  
 $\alpha$ -Nitro- $\alpha$ -phenylacetophenone -o-Carboxylic Acid

ASSOCIATION: Institut biologicheskoy i meditsinskoy khimii Akademii  
meditsinskikh nauk SSSR (Institute of Biological and Medical  
Chemistry of the Academy of Medical Sciences, USSR)

SUBMITTED: July 13, 1957

Card 3/3

5(3)

SOV/20-128-1-30/58

AUTHORS: Shemyakin, M. M., Academician, Kolosov, M. N., Arbuzov, Yu. A.,  
Hsieh lu-yuan, Sheng Hui-yü, Sklobovskiy, K. A.,  
Karapetyan, M. G., Gurevich, A. I.

TITLE: Intermediate Stages in the Synthesis of Tetracyclines

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 128, Nr 1, pp 113-116  
(USSR)

*Info No 4 June 1958*

ABSTRACT: In 1956 the authors synthesized tricyclic ketols of kind (I) (Ref 1). They are similar to tetracyclines (III) as far as the structure of two rings is concerned. In the third ring they have a reactive double linkage in position 2,3. The present paper investigates the addition of heterogeneous reagents to the 2,3-double linkage of compounds (I) for introducing active groups into their molecules. The active groups are necessary for establishing a  $\gamma$ -grouping (II) in the B-ring and for a further extension of the A-ring of tetracyclines by a method previously elaborated. Investigations have shown that compounds (I) with typical electrophilic reagents such as  $\text{Hal}_2$ ,  $\text{RCO}_3\text{H}$  and  $\text{HOHal}$  react readily. Thus, corresponding

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halogen derivatives, epoxides, hydride halides, and halogen

SOV/20-128-1-30/58  
Intermediate Stages in the Synthesis of Tetracyclines

ketones with good yields are formed. Constants and analytical results of synthesized compounds are given in table 1. The synthesis of tricyclic ketols with active groups in the B-ring made by the authors provides the possibility of building up the A-ring of tetracyclines. There are 1 table and 3 references, 2 of which are Soviet.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo AN SSSR  
(Institute of Organic Chemistry imeni N. D. Zelinskiy, AS USSR).  
Institut biologicheskoy i meditsinskoy khimii AMN SSSR  
(Institute of Biological and Medical Chemistry, AMN USSR)

SUBMITTED: June 4, 1958

Card 2/2

(3)

AUTHORS: Shemyakin, M. M., Lur'ye, M. Yu.

SOV/79-29-8-15/81

TITLE: Investigations of the Chemistry of Chloromycetin (1 Mycetin).  
IX. Synthesis of the New Analog of Chloromycetin (D-TREO-1-  
(n-formylphenyl)-2-dichloroacetylamino-1,3-propanediol)

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 8, pp 2531 - 2533  
(USSR)

ABSTRACT: *Submitted 11 July 1958*  
Of the analogs of chloromycetin (I, R=CHCl<sub>2</sub>) this hitherto un-  
described analog is of special importance (IV, X=CHO; R=CHCl<sub>2</sub>).  
The presence of the aldehyde group within it allows for the  
synthesis of a large number of other hitherto little accessible  
chloromycetin analogs, which are important for the further ex-  
planation of the varied dependence of the antimicrobial activity  
on the structure of these compounds. On the basis of the method  
elaborated by W. F. Beech (Ref 2) for the introduction of the  
aldehyde group into the aromatic ring by way of diazo compounds,  
the authors succeeded in applying the simple synthesis of op-  
tically active chloromycetin analogs (IV, R=CHCl<sub>2</sub>) directly from  
chloromycetin (I, R=CHCl<sub>2</sub>), suggested by them (Ref 3), for the

Card 1/3

Investigations of the Chemistry of Chloromycetin (1-Mycetin). IX. Synthesis of the New Analog of Chloromycetin (D-TREO-1-(n-formylphenyl)-2-dichloroacetyl-amino-1,3-propanediol) SOV/79-29-8-15/81

synthesis of the aldehyde they were interested in (Schemes). Initially, the transformation did not proceed from compound (I) but from its racemic N-benzyl analog (I, R=C<sub>6</sub>H<sub>5</sub>), since in this way crystallizing compounds are more easily obtained. With it, the diazo group was replaced by the aldehyde group in compound (III, R=C<sub>6</sub>H<sub>5</sub>) under conditions suggested by Beech (Ref 2) as an optimum. Compound (IV, X=CHO; R=C<sub>6</sub>H<sub>5</sub>) was easily separated in crystalline form (yield 15%). This aldehyde was then characterized in the form of the 2,4-dinitrophenyl hydrazone and other derivatives. The synthesis of compound (IV, X=CHO; R=CHCl<sub>2</sub>) proceeded more difficultly. It was synthesized as above from compound (III, R=CHCl<sub>2</sub>). However, it was not possible to obtain it in crystalline state even after careful purification. This aldehyde was characterized in the form of the 2,4-dinitrophenyl hydrazone (yield 12%). There are 3 references; 2 of which are Soviet.

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Investigations of the Chemistry of Chloromycetin SOV/79-29-8-15/81  
Chloromycetin). IX. Synthesis of the New Analog of  
Chloromycetin (D-TREO-1-(n-formylphenyl)-2-dichloroacetyl-amino-1,3-propanediol)

ASSOCIATION: Institut biologicheskoy i meditsinskoy khimii Akademii  
meditsinskikh nauk SSSR (Institute of Biological and Medical  
Chemistry of the Academy of Medical Sciences, USSR)

SUBMITTED: July 11, 1958

Card 3/3

0.3400, 0.3400, 0.3410

77017  
001/72-59-12-21/43

AUTHORS: Shemyakin, M. M., Ravdel', G. A., Chaman, E. S.,  
Shvetsov, Yu. B., Vinogradova, E. I., Vdovina, R. G.,  
Yermolayev, K. M., Bamdas, E. M.

TITLE: Studies in the Field of Sarcosine and Its Analogs.  
Communication 4. Study of Synthetic Routes to Sar-  
cosine and Its Analogs

PERIODICAL: Investiya Akademii nauk SSSR. Otdeleniye khimicheskikh  
nauk, 1959, Nr 12, pp 2177-2187 (USSR)

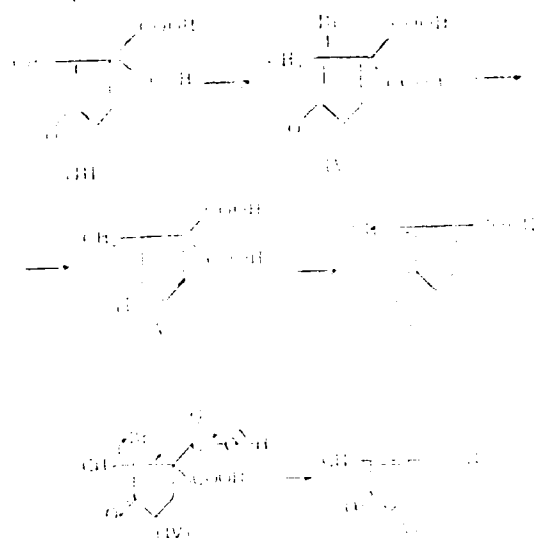
ABSTRACT: *12 Dec 1958*  
2-Methylcyclopentan-3-one-1,1-dicarboxylic acid (III)  
was used for the preparation of (Sarcosine) 2-methyl-  
cyclopentanone-3-carboxylic acid (I). (III) was  
assumed to be converted into (V) by bromination. It  
seemed possible to synthesize (I) from (V) by removal  
of HBr and by decarboxylation. Diacid (II) could not  
be obtained because elimination of HBr from (II) and  
simultaneous decarboxylation formed (VI) with an  
endocyclic double bond.

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Studies in the Field of Sarcosine and  
Its Analogs. Communication 4. Study of  
Synthetic Routes to Sarcosine and Its  
Analogues

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Card 2/10

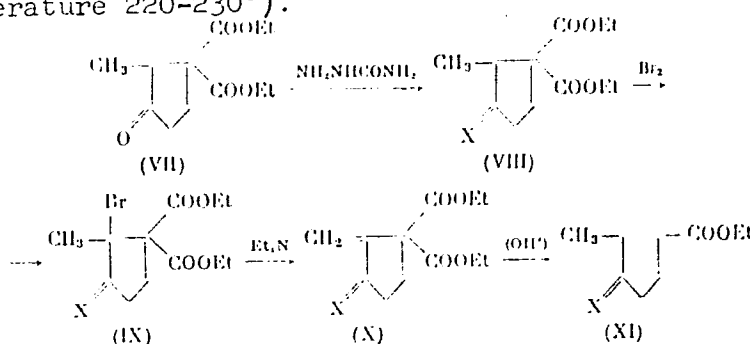


Studies in the Field of Sarcomycine and Its Analogs. Communication 4. Study of Synthetic Routes to Sarcomycine and Its Analogs

77077

SOV/62-59-12-21/43

The semicarbazone of the diethyl ester of 2-methylcyclopentan-3-one-1,1-dicarboxylic acid (VIII) was brominated, and after eliminating HBr the semicarbazone of the diethyl ester of 2-methylenecyclopentan-3-one-1,1-dicarboxylic acid (X) was obtained in 56% yield (mp 207-209°). Diester (X) was saponified and the semicarbazone of the ethyl ester of 2-methylcyclopenten-1-one-3-carboxylic acid (XI) was obtained, in 74% yield (dec. temperature 220-230°).



where X = NNHCONH<sub>2</sub>.

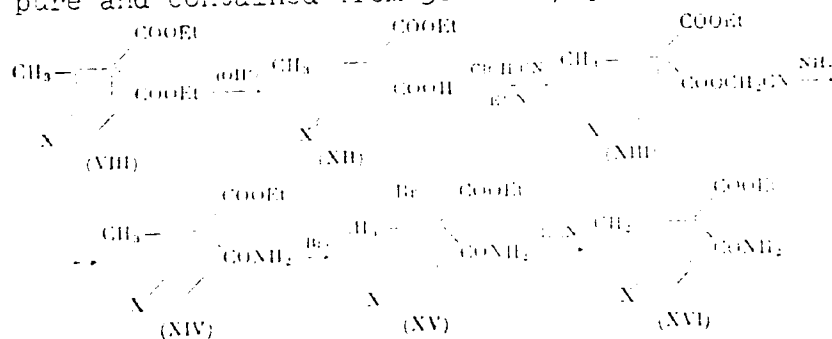
Card 3/10

Studies in the Field of Sarcomycine and Its Analogs. Communication 4. Study of Synthetic Routes to Sarcomycine and Its Analogs

77077

SOV/62-59-12-21/43

Attempts were made to convert the semicarbazone of the amide of 1-carbethoxy-2-methylcyclopentanone-3-carboxylic acid (XIV) into the semicarbazone of the amide of 1-carbethoxy-2-methylenecyclopentanone-3-carboxylic acid (XVI), but the isolated compound (XVI) was not pure and contained from 30 to 40% polymeric material.



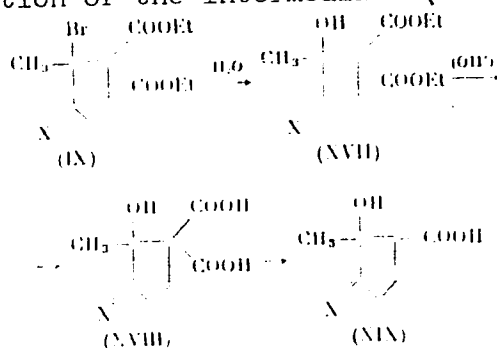
Card 4/10

Studies in the Field of Sarcomycine and Its Analogs. Communication 4. Study of Synthetic Routes to Sarcomycine and Its Analogs

77077

SOV/62-59-12-21/43

Semicarbazone of the diethyl ester of 2-methylcyclopentan-2-olone-3-carboxylic acid (XVII) was obtained, in 81% yield (mp 160-161<sup>o</sup>), from (IX) by reaction with water. Semicarbazone of 2-methylcyclopentan-2-olone-3-carboxylic acid (XIX) was prepared in 38% yield (mp 187-188<sup>o</sup>) by saponification of (XVII) and by subsequent decarboxylation of the intermediate (XVIII).

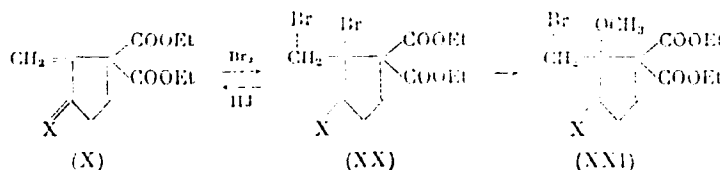


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Studies in the Field of Sarcomycine and  
Its Analogs. Communication 4. Study of  
Synthetic Routes to Sarcomycine and Its  
Analogues

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207/62-59-12-21/43

Dibromide (XX) was obtained quantitatively (mp 82-85° dec.) by addition of two bromine atoms to the diester (X). In the compound (XX) one bromine atom (position 2) is very labile. (XX) reacts with CH<sub>3</sub>OH or H<sub>2</sub>O forming corresponding compounds (XXI) in 65% yield (mp 138-139°) or (XXII) in 83% yield (mp 148-149°). The labile bromine atom in compound (XX) can quantitatively oxidize KI to free iodine, in the cold, but the obtained product can not be isolated, because the reaction is accompanied by elimination of HBr and formation of diester (X) in 71% yield (mp 207° dec.).

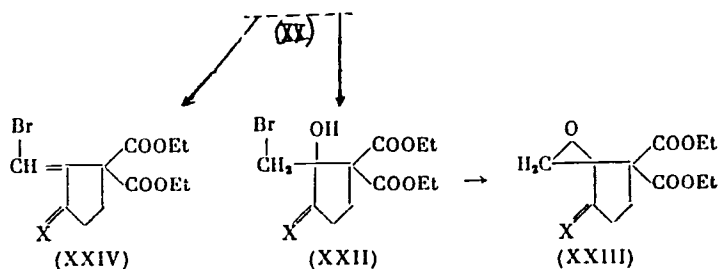


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Studies in the Field of Sarcomycine and Its Analogs. Communication 4. Study of Synthetic Routes to Sarcomycine and Its Analogs

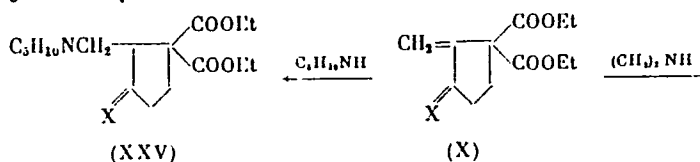
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SOV/62-59-12-21/43



where  $X = \text{NNHCONH}_2$ .

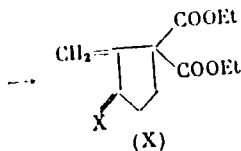
Compound (X) was converted into corresponding amines (XXV), in 17% yield (mp 124-126°), and (XXVI), in 62% yield (m p 160-161°), according to the reaction:



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Studies in the Field of Sarcomycine and Its Analogs. Communication 4. Study of Synthetic Routes to Sarcomycine and Its Analogs

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SOV/62-59-12-21/43



where X = NNHCONH<sub>2</sub>.

The synthesis of (I) may take place as follows: amines of (XXV-XXVI)-type, after hydrolysis, decarboxylation, and formation of the methylene group, can be converted into (I). The results of investigation will be published in a forthcoming communication. There are 9 references, 3 Soviet, 1 German, 2 Japanese, 1 U.K., 2 U.S. The 3 U.S. and U.K. references are: Chem. and Industr. 1957, 1320; E. J. Corey, J. Amer. Chem. Soc. 75, 1163 (1953); J. R. Hooper, L. C. Cheney et al., Antibiot. and Chemother. 5, 585 (1955).

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Studies in the Field of Sarcomycine and  
Its Analogs. Communication 4. Study of  
Synthetic Routes to Sarcomycine and Its  
Analogs

77077  
SOV/62-59-12-21/43

ASSOCIATION: Institute of Biological and Medical Chemistry, Academy  
of Medical Sciences (Institut biologicheskoy i meditsinskoy khimii Akademii medicinskikh nauk)

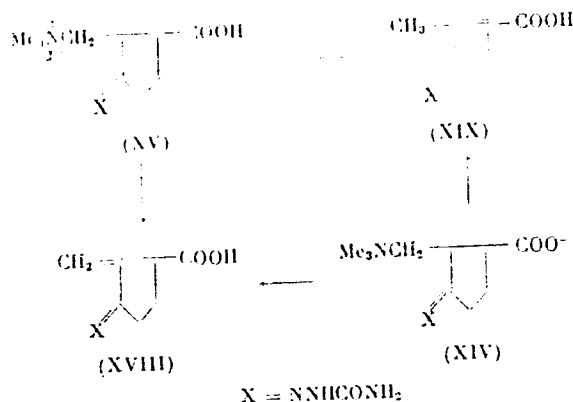
SUBMITTED: April 12, 1958; Additions made, December 28, 1958

Card 10/10

Investigation in the Field of Sarcomycine  
and Its Analogs. Communication 5. Synthesis  
of Racemic Sarcomycine

77078

SOV/62-59-12-22/43



The ethyl ester of 2-dimethylaminomethylcyclopentanone-3-carboxylic acid (XI) was used as starting material for the preparation of (III). Racemic sarcomycine in the form of its semicarbazone (XVII) can be obtained, in 39% yield, from the methiodide of acid (XV) or from betaine (XIV) together with the semicarbazone of 2-methylcyclopenten-1-one-3-carboxylic acid (XIX). For

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Investigation in the Field of Sarcomycine  
and Its Analogs. Communication 5. Synthesis  
of Racemic Sarcomycine

77078

301/62-59-12-12/43

this purpose (XV) or (XIV) is heated on a water bath for 4 minutes with 2 moles (for betaine 1 mole) of 1N NaOH. The solution was cooled to 0-20°, 10% HCl was added, and after 30 minutes the precipitate was removed by filtration and washed with cold water. The mixture of (XVIII) and (XIX) was obtained in 39% yield. The compound turns black on heating, but does not melt. Found: C 48.87%; H 6.02%.  $C_8H_{11}O_3N_3$ . Calculated: 48.75%; H 5.63%. From the above mixture, the semicarbazone of racemic sarcomycine (XVIII) was isolated by crystallization, in 50-55% yield. There are 3 references, 3 Soviet, 1 Japanese, 1 U.K., 3 U.S. The 4 U.S. and U.K. references are: Chem. and Industr. 1957, 1320. G. Buchi, N. G. Yang and Others, Chem. and Industr. 1953, 1063; J. Meinwald, S. L. Emerman and others., J. Amer. Chem. Soc. 77, 2401 (1955); E. E. Van Tamelen, S. R. Bach, J. Amer. Chem. Soc. 77, 4683 (1955).

Card 3/4

Investigation in the Field of Sarcosine  
and Its Analogs. Communication 5. Synthesis  
of Racemic Sarcosine

77078  
S07/52-59-12-22/43

ASSOCIATION: Institute of Biological and Medical Chemistry, Academy  
of Medical Sciences (Institut biologicheskoy i meditsin-  
skoy khimii Akademii meditsinskikh nauk)

SUBMITTED: April 12, 1958; Additions made, December 28, 1958

Card 4/4

5 (3)

AUTHORS:

Shemyakin, M. M., Kolosov, M. N.,  
Arbuzov, Yu. A., Karapetyan, M. G.,  
Chaman, Ye. S., Onishchenko, A. A.

SOV/29-6-13/72

TITLE:

Investigations in the Field of Tetracyclines (Issledovaniya v oblasti tetratsiklinov). IV. Investigation of Different Syntheses of the Tricyclic System DCB of the Tetracyclines (IV. Izucheniye putey sinteza tritsiklicheskoy sistemy DCB tetratsiklinov)

PERIODICAL:

Zhurnal obshchey khimii, 1959, vol 29, Nr 6, pp 1831 - 1842 (USSR)

ABSTRACT:

*See entry 1/3*  
The structure of the well-known tetracyclines (I) has a specific characteristic which indicates the ways and methods necessary for carrying out the complete synthesis of compounds of this type. On the basis of certain theoretical considerations the authors tried to synthesize such ketols of the hydroanthracene series of type (III) and (IV) in which two rings had to be similar with respect to structure and spatial arrangement to the rings D and C of the tetracyclines. The third ring had to offer the structural conditions for the subsequent building-up of the ring A and for the introduction of the necessary func-

Card 1/3

Investigations in the Field of Tetracyclines.  
IV. Investigation of Different Syntheses of the  
Tricyclic System DCB of the Tetracyclines

SOV/79-29-6-13/72

tional groups of the ring B of the tetracyclines. The adopted method of synthesizing these compounds consisted in the condensation of the 1,4-naphthoquinones with butadiene or its derivatives and the transformation of the resultant adducts (II) into the ketols (III) which, on their part, can easily be hydrolyzed to give the oxy-diketones (IV). The first step, the diene synthesis, takes place readily by heating naphthoquinone with the diene. By condensation of the 5-methoxy-naphthoquinone with 2-methoxy-butadiene two isomeric adducts - (II d) and (II e) in the ratio 4 : 1 - are formed. The second step, the selective transformation of the C<sub>9</sub>-keto group of the adducts (II) into the tertiary methyl carbinol grouping meets with some difficulties, it was however possible to carry out the reaction by means of magnesium methyl halide. The third step of the synthesis of the compounds (IV), the hydrolysis of the enol-methoxyl up to the keto group is only possible when using dilute acids. The synthesis of the tricyclines (XV) was thus performed on the basis of naphthoquinones, in which two rings are analogous with the rings D and C of the natural tet-

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Investigations in the Field of Tetracyclines.  
IV. Investigation of Different Syntheses of the  
Tricyclic System DCB of the Tetracyclines

SOV/79-29-6-13/72

racyclines with respect to structure and spatial arrangement. The presence of the reactive double bond, the enol grouping or the carbonyl group on the third ring of the compounds (XV) offers further possibilities for the introduction of substituents and for the building up of the fourth ring of the tetracyclines. There are 12 references, 4 of which are Soviet.

ASSOCIATION: Institut biologicheskoy i meditsinskoy khimii Akademii meditsinskikh nauk SSSR i Institut organicheskoy khimii Akademii nauk SSSR (Institute of Biological and Medical Chemistry of the Academy of Medical Sciences, USSR, and Institute of Organic Chemistry of the Academy of Sciences, USSR)

SUBMITTED: June 9, 1958

Card 3/3

5(2, 3)

S07/20-128-3-36/58

AUTHORS:

Shemyakin, M. M., Academician, Maymind, V. I., Yermolayev, K. M., Bamdas, E. M.

TITLE:

On the Reaction Mechanism of Osazone Formation

PERIODICAL:

Doklady Akademii nauk SSSR, 1959, Vol 128, Nr 3, pp 564-566(USSR)

ABSTRACT:

In spite of many investigations (Refs 1-15), the formation of osazones from  $\alpha$ -oxycarbonyl compounds remains unclear. All respective hypotheses and assumptions can be reduced to 3 schemes: A (Ref 1), B (Ref 3), and C (Ref 3). In order to find the correct scheme, the osazone reaction was marked with  $^{15}\text{N}$ . If scheme A applies, the resulting ammonia may not contain an excess in  $^{15}\text{N}$ , but the  $^{15}\text{N}$  must completely remain in the osazone. If, however, scheme B is correct, the osazone will remain unmarked while the ammonia will contain the entire marking. Finally, if scheme C is the right one, the  $^{15}\text{N}$  excess will be distributed, in equal shares, between osazone and ammonia. Unfortunately, the investigation of the mechanism under discussion by means of tagged atoms is much impeded by the fact that the marking may be diluted by exchange reactions, hydrolysis or substitution. These secondary processes could be avoided to a large extent, by producing the osazones in boiling isoamyl alcohol and removing the water from the reac-

Card 1/3

On the Reaction Mechanism of Osazone Formation

SOV/20-128-3-36/58

tion sphere. Then, the dilution of the marking in the hydrazone is inconsiderable at the beginning, and cannot conceal the reaction mechanism of osazone formation. Therefore, it can be rather accurately judged which of the 3 schemes really applies. For this purpose, the reaction must be interrupted after a certain period (depending on the type of hydrazone used). The investigations were carried out with  $\beta$ - $^{15}\text{N}$ -p-nitrophenyl hydrazones of fructose, cyclohexanone and benzoin. Boiling alcoholic solutions of the said hydrazones and of an unmarked p-nitrophenyl hydrazine (2 moles) were poured together, and subsequently boiled in the nitrogen current. The resulting ammonia was immediately removed from the reaction solution. The isolation and separation of osazone, hydrazone and hydrazine was done as quickly as possible under conditions which prevent a further change in the marking by exchange reactions. As they could not be fully eliminated, it was more convenient to measure the isotopic composition of ammonia, not of osazone. Table 1 shows that the escaping ammonia at first always contained much more than half of the marking of the initial hydrazone. Hence it is concluded that scheme B applies to all cases investigated. This scheme is distinguished from the others by the fact that the 1st reaction stage proceeds without par-

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On the Reaction Mechanism of Osazone Formation SOV/20-12873-36/58

precipitation of hydrazine. As was expected, it could be observed that the osazone-formation process can be divided into 2 stages with separation of an intermediate monoimine of  $\alpha$ -diketone (I). By the example of p-nitrophenyl hydrazone of benzoin, it was ascertained that prolonged heating at 60° in glacial acetic acid and without hydrazine causes its disappearance. If 2 moles of hydrazine are subsequently added, an osazone precipitation is quickly formed. There are 1 table and 15 references.

ASSOCIATION: Institut biologicheskoy i meditsinskoy khimii Akademii meditsinskikh nauk SSSR  
(Institute of Biological and Medical Chemistry of the Academy of Medical Sciences, USSR)

SUBMITTED: June 22, 1959

Card 3/3



Investigation of the Methods of Ring Synthesis of  
A-Tetracyclines - Method of Introducing the N,N-Di-  
methylglycine Residue Into the Cyclohexanone Ring

SOV/20-128-4-30/65

these problems. A model synthesis and some transformations of the simplest compound of type (IVb) - the ester of threo-2-keto-cyclo-hexyl-N,N-dimethyl glycine (XIIa) - are described. The above-mentioned introduction into the cyclohexanone ring has to be carried out under such conditions and by such methods as are also applicable to the case of tricyclic oxydiketones (I). This method is described. The authors ascribed a threo-configuration to the dimethyl-amino-keto ester obtained. This was also confirmed by further transformations (XVIII) and (XIVa). Table 1 shows the compounds obtained, their constants, as well as the composition found analytically and by computation (VIa - XXII). The dimethyl-amino-keto ester (XIIa) synthesized by the authors was also investigated with respect to the introduction of an ethinyl residue into the molecule. This is necessary for building up the "lower" part of the A-ring of tetracyclines by the method developed previously (Ref 2). It was shown that (XIIa) easily reacts with  $\text{HC} \equiv \text{CNa}$  in liquid  $\text{NH}_3$  at  $-50^\circ$  to form an acetylene-oxy ester in a 60% yield. The latter is supposed to

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SOV/79-29-9-1/76

5(3)

AUTHORS: Semenov N. N., Shemyakin, M. M., Kochetkov, N. K.

TITLE: Academician Aleksandr Nikolayevich Nesmeyanov. (On His 60th Birthday)

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 9,  
pp 2811 - 2816 (USSR)

ABSTRACT: A. N. Nesmeyanov (born 9.9.1899 in Moscow) graduated from the Physical and Mathematical Department of Moscow University in 1922, became an assistant to the well-known chemist N. D. Zelinskiy, and later was appointed professor in ordinary and head of the Chair of Organic Chemistry; he attained the highest degree in 1947, when he was elected rector. He became a member of the Academy of Sciences in 1943, and of other institutions later on. An outstanding speaker, he has a special talent of rendering the most complicated subjects intelligible and pleasant. His activities have covered various fields, from a great number of problems belonging to elemental-organic chemistry to the synthesis of valuable new polymers, from theoretical problems of reaction mechanism and reactivity to the introduction of methods of synthesis relating to the compound

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Academician Aleksandr Nikolayevich Nesmeyanov.  
(On His 60th Birthday)

SOV/79-29-9-1/76

heterocyclic systems. Among his numerous achievements the following deserve first mention: the simple method of synthesizing metal-organic compounds by the aid of aromatic diazocompounds, a method which is still regarded as the best for the synthesis of aromatic derivatives of mercury, antimony, arsenic. This method has been developed to apply to syntheses of aromatic compounds of tin, zinc, thallium, aluminum as well as organomercury-silver compounds from compounds of Sn, Pb, As, Sb, Cd, Tl, and others. Remarkable syntheses are the ones yielding iodonium-, bromonium-, and chloronium compounds, and finally, oxonium compounds by the arylation of bromo- and chlorobenzene, and of diphenyl ether with diazonium borofluoride. Great importance has been and still is attached to his investigations concerning the addition of metals to the unsaturated compounds of the olefin and acetylene series, the exchange of metal atoms in the compounds of the above metals containing a  $\beta$ -chlorovinyl radical. Nesmeyanov has developed a new conception of the manifold reactivity and displacement of the reaction center in the reactions of metal compounds. His attempt of solving

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Academician Aleksandr Nikolayevich Nesmeyanov.  
(On His 60th Birthday)

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the problem of the mechanism of electrophilic substitution on the saturated carbon atom deserves special mention. He investigated the metallocenes, metal-organic compounds formed by the interaction of the s,p,d-electrons of the transition metals with the  $\pi$ -electrons of the unsaturated carbon bonds. The aromatic nature of ferrocene was proven by numerous reactions. From 1938 to 1954, Nesmeyanov was the head of the Institut organicheskoy khimii AN SSSR (Institute of Organic Chemistry AS USSR), from 1954 head of the Institut elemento-organicheskikh soyedineniy AN SSSR (Institute of Elemental-organic Compounds AS USSR); 1946-48, secretary of the Otdeleniye khimicheskikh nauk AN SSSR (Department of Chemical Sciences AS USSR), and since 1951 he is the President of the Akademiya nauk SSSR (Academy of Sciences, USSR). Since 1947 he is the chairman of the committee presiding over the scientific Lenin Prize awards (formerly called Stalin Prize). He was distinguished with the Lenin Order, the Order of the Red Workers' Banner, and the Stalin Prize First Class for scientific merits.

Card 3/3

11  
20.11.1986/15

Author: Leontyev, A. E., Arbutov, Yu., Potolov, B. N., Gerasimov, G. A., Gerasimov, V. V., Potolov, Yu. V.

Topic: Reaction of Dimers of Tetrahydro- 71. On the Reaction of Dimers with Hydrogen

Reference: Zhurnal Obshchei Khimii, 1980, Vol. 50, No. 2, pp. 31-35 (USSR)

Abstract: Hydrogenation of dimers with various substituents and for one of the following variants: There are 3 references, 1 Soviet, 1 German, 1 U.S. The U.S. reference is: R. L. Frank, H. K. Hall, J. Am. Chem. Soc., 72, 1641 (1950).

Annotation: Institute of Organic Chemistry, Academy of Sciences, USSR (Institut organicheskoy khimii Akademiya Nauk SSSR)

Keywords: Reaction, 15, 15

0.3010

77886

SOV/79-30-2-37/78

AUTHORS: Shemyakin, M. M., Kolosov, M. N., Arbuzov, Yu. A.,  
Onoprienko, V. V., Sich Yd-yllan

TITLE: Investigation in the Field of Tetracyclines. VII.  
Study of the Synthetic Routs to the A Ring of  
Tetracyclines

PERIODICAL: Zhurnal obshchey khimii, 1960, Vol 30, Nr 2,  
pp 545-550 (USSR) *Submitted 25 Feb 1959*

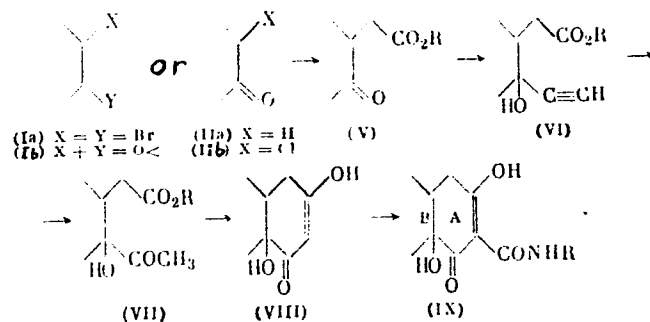
ABSTRACT: Synthesis of compound IX can be divided into three  
parts: (1) construction of the upper parts of the  
A ring (Ia (Ib) or IIa (IIb)  $\rightarrow$  (V)); (2) construction  
of its lower parts (V  $\rightarrow$  VI  $\rightarrow$  VII); and cyclization with  
subsequent introduction of carboxamide group (VII  $\rightarrow$   
VIII  $\rightarrow$  IX).

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Investigation in the Field of Tetracyclines.  
VII. Study of the Synthetic Route to the A  
Ring of Tetracyclines

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SOV/79-30-2-37/78

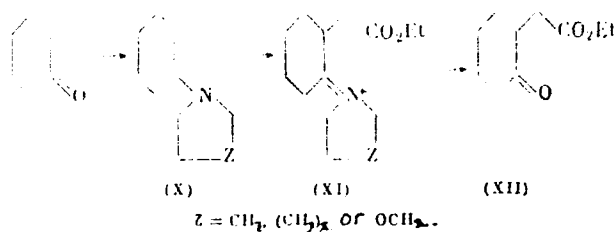


The following compounds can be used for construction of the upper ring: dibromides (Ia); epoxides (Ib); ketones (IIa); and haloketones (IIb). The third way (IIa) is simpler.

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Investigation in the Field of Tetraacyclines.  
VII. Study of the Synthetic Route to the A  
Ring of Tetraacyclines

TS-11  
SC-75-30-2-37-78



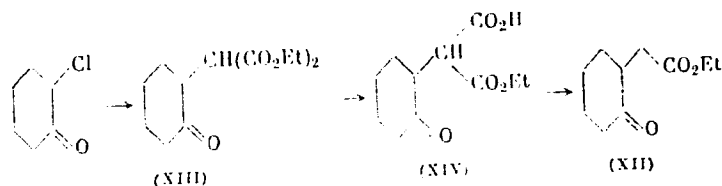
The fourth way (I.b) puts the carbomethoxy group exclusively in a certain position of cyclohexane ring.

Card 3/11

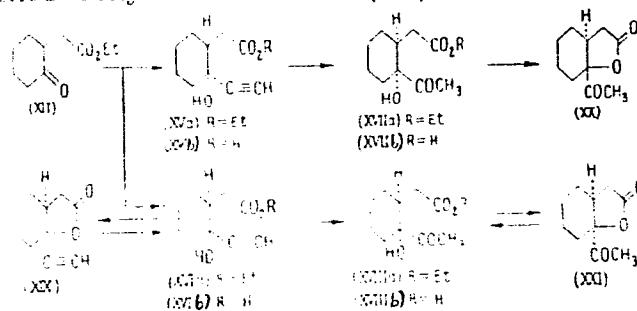


Investigation in the Field of Tetracyclines.  
VII. Study of the Synthetic Route to the A  
Ring of Tetracyclines

77866  
30V/72-33-2-37/70



Construction of lower parts of the A ring includes  
ethynylation of V and hydration of the triple bond of  
the obtained ethynyl carbinol (VI).



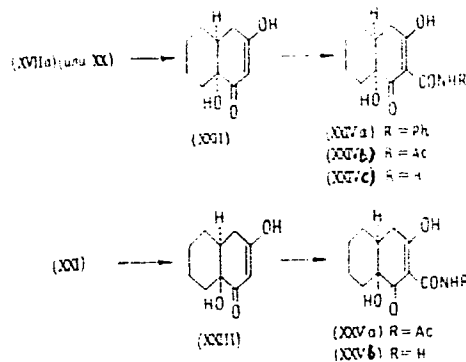
Card 4/11

Investigation in the Field of Tetracyclines.  
VII. Study of the Synthetic Route to the A  
Ring of Tetracyclines

77085

30770-30-2-37,78

Na-enolates of hydroxydiketones react in dimethyl-  
formamide with excess of the corresponding isocyanate  
(carboxyamidation of hydroxydiketones XXII and  
XXIII).



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Investigation in the Field of Tetracyclines.  
VII. Study of the Synthetic Route to the A  
Ring of Tetracyclines

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SOV/79-30-2-37/78

Some Properties of Obtained Products

Nr	Starting Material	Obtained Product	Yield (%)	bp, mm pr	$n_D^{(x)}$
1	Cyclohexanone + secondary amine toluenesulfonic acid + benzene	X	-	-	-
2	X + bromoacetic ester XII + hydrolysis with aqueous methanol		-	121-122°/7	x = 18 1.4592
3	Sodium malonic ester XIII + 2-chlorocyclohexanone + malonic ester + benzene	XIII	70	151-153°/3	x = 20 1.4595

piperidine, pyrrolidine, morpholine.

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Investigation in the Field of Tetracyclines.  
VII

77880  
SCV/79-30-2-37/78

Nr	Starting Material	Obtained Product	Yield (%)	bp/mm pr	$n_D^{(x)}$
4	Saturated HC≡CH solution in liquid ammonia + Na + XII + abs. ether + NH <sub>4</sub> Cl	mixture of XV-a and XVI-a	85	83-84°/0.02	x = 18 1.4831
5	Mixture of XVa and XVI-a are hydrolyzed with NaOH	XV-b + mother liquid	71	mp 101-2°	-
6	the above mother liquid (5) + 0.1N H <sub>2</sub> SO <sub>4</sub>	XIX	24	63-64°/0.04	x = 21 1.4926
7	XIX is hydrolyzed with 0.1 N NaOH, acidified with 1 N H <sub>2</sub> SO <sub>4</sub> , and extracted with CHCl <sub>3</sub>	XVI-b	-	-	-

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Investigation in the Field of Tetracyclines.  
VII.

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Nr	Starting Material	Obtained Product	Yield (%)	bp/mm pr	$n_D^{(x)}$
8	Mixture of XVa and XVIa + anhydrous alcohol + mercuric acetate	mixture of XVII-a and XVIII-a	66	90-92°/0.03	x = 17 1.4735
9	Mixture of XVa and XVIa + mercuric salt of p-toluenesulfon- amide + alcohol	mixture of XVII-a and XVIII-a	41	-	-
10	Mixture of XVIIa and XVIIIa + alcohol + hydrolysis with 0.4 N NaOH	XVII-b + mother liquid	72	mp 115-6°	-
11	The above mother liquid (10) is boiled with 1 N H <sub>2</sub> SO <sub>4</sub>	XXI	24	72-73°, 0.03	-

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Investigation in the Field of Tetracyclines.  
VII

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SOV/79-30-2-37/76

Nr	Starting Material	Obtained Product	Yield (%)	bp/mm pr	$n_D^{(x)}$
12	XXI is hydrolyzed with 0.1 N NaOH	XVIII-b	96	mp 98-100°	-
13	XVII-b is heated at 150°/15 mm	XX	91	70-71°/0.12	x = 22 1.4828
14	XVIII-b + Na <sub>2</sub> CO <sub>3</sub> + AgNO <sub>3</sub> + ethyl iodide	XVII-a	90	91-92°/0.03	x = 19 1.4737
15	XVII-b or XVIII-b is distilled at 130°/0.07	XVIII-b trans in 88 the form of lactone	-	-	-

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Investigation in the Field of Tetracyclines,  
VII

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Nr	Starting Material	Obtained Product	Yield (%)	bp/mm pr	$n_D^{(x)}$
16	XVII-b or XXVIII-b + 0.1 N $H_2SO_4$ after 2 hours	XVIII-b in the form of lactone	100	-	-
17	XVII-a + 0.5 N sodium ethoxide in alcohol	XXII (cis)	95	mp 181-182°	-
18	XXII (cis) + di- methylformamide + phenylisocyanate	XXIV-a	46	-	-
19	XXIV-b + $NH_3$ + $CH_3OH$	XXIV-b (cis)	75	mp 153-154°	-
20	XXV-a + ammonolyse	XXV-b (trans)	65	mp 160-161°	-

Card 10/11

SHEMYAKIN, Mikhail M.

"Synthesis of Depsipeptides."

report to be submitted for the Symposium on the Chemistry of Natural Products,  
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Prof. Act. Mbr., Acad. Sci. USSR  
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866-871 My '60. (MIRA 13:6)

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BERGEL'SON, L.D.; VAYER, V.A.; SHEMYAKIN, M.M.

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